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Rapid Vulcanization of Saturated Acrylic Elastomers[1]

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CONVERSION of acrylic resins into rubbery vulcanizates, designated Lactoprene, was described in a previous paper.[3] Although several methods of vulcanizing non-olefinic polymeric acrylic esters were reported, vulcanization was not sufficiently rapid; two or more hours were required for all recipes except that based on benzoyl peroxide. Curing with benzoyl peroxide was rapid, but the products were not so strong as those obtained with other agents. Development of more rapid vulcanization procedures was undertaken in this laboratory because it is highly advantageous commercially to achieve vulcanization in 30 minutes or less, and it was considered likely that vulcanizates produced in 15 to 30 minutes would have properties different from those made by slow vulcanization. Results of this investigation and miscellaneous observations regarding the preparation and properties of vulcanized acrylic resins are described in the present paper.

Halogen-containing acrylic polymers were used in seeking rapid vulcanization methods, primarily because such polymers can be made readily and vulcanized by various recipes.[3] Advantages of preparing and vulcanizing saturated rather than olefinic acrylic polymers have been described.[3]

Experimental Details

The acrylic copolymers were prepared by emulsion polymerization, generally according to the procedures previously described.[3,4] Ethyl acrylate was used as the principal monomer because of its availability and the rubbery characteristics of its polymers. Halogen-containing acrylic resins were prepared conveniently by copolymerizing ethyl acrylate with chloro- or bromo-alkyl acrylates, whose preparation by alcoholysis[5] and properties will be described elsewhere. At the end of the polymerization, steam was passed through the emulsion to distill monomer and impurities, and coagulation was effected by addition of an aqueous solution of sodium chloride. The polymers were washed with water on a washing mill and air-dried.

Satisfactory results have been obtained by freeing the monomers of the inhibiter (hydroquinone) by several washings with dilute sodium hydroxide and water, but separation by distillation seemed preferable, and in most instances the acrylic esters were redistilled before polymerization.

Although milling characteristics of acrylic polymers are distinctly different from those of natural rubber, polyethyl acrylate and similar acrylic elastomers can be readily and rapidly milled without softeners or plasticizers. Because of their saturated character, the usual preliminary milling to cause "breakdown" is omitted, and the compounding ingredients are added as soon as the polymer is placed on the rolls. Temperature is not critical, but 125° F. (52° C.) was generally used in this work. Although the polymer sometimes adheres to both rolls in the beginning, the ingredients are added rapidly without any effort to force the polymer to go on one roll. Toward the end of the milling, the polymer usually migrates to the front roll, from which it is readily removed.

When plasticizers are milled into acrylic resins, it is advantageous in some instances to incorporate small portions of reenforcing agent and plasticizer intermittently.

The following accelerators[6] and other agents were used: calcined magnesia (extra-light calcined magnesia); Captax (mercaptobenzothiazole); Cumate (copper salt of mercaptobenzothiazole);[7] Du Pont No. 8 (formaldehyde-p-toluidine product); Furnex beads (semi-reenforcing carbon black); GMF (quinone dioxime); Kalvan (small particles of coated calcium carbonate); Kosmos 40 (special reenforcing furnace black); Micronex (channel black); Monex (tetramethyl thiuram monosulphide); phenylstearic acid (prepared by interaction of oleic acid and benzene and supplied by the oil and fat division of this Laboratory; Polyac (agent used by Sturgis and Trepagnier)[8]; R2 crystals (reaction product of carbon disulphide and methylenedipiperidine); Rotax (mercaptobenzothiazole); Safex (2,4 dinitrophenyl dimethyldithiocarbamate); Selenac (selenium diethyldithiocarbamate); Tergitol Penetrant Paste No. 4 (sodium tetradecyl sulphate, 50%)[9]; Triton 720 (sodium salt of aryl alkyl polyether sulfonate)[9]; Tuads (tetramethylthiuram disulphide); and 2MT (2-mercaptothiazoline).

The compounded mixtures were cured in stainless-steel sandwich molds having the dimensions 4- by 4- by 0.032-inch or standard A.S.T.M. molds (6- by 6- by 0.075-inch). As a rule, cellophane sheets were used in the smaller mold. Results obtained by vulcanizing a 95% ethyl acrylate-5% 2-chloroethyl acrylate copolymer in the large and small molds (Table 1) indicate that curing occurs somewhat more rapidly in the smaller mold.

TABLE 1. VULCANIZATION OF 95% ETHYL ACRYLATE-5% 2-CHLOROETHYL ACRYLATE COPOLYMER* IN LARGE AND SMALL MOLDS†

Expt. No.	Vulcanization Recipe	Mold	Curing time at 298°F., Minutes	Tensile P.S.I.	Ultimate Elongation %	Shore A Hardness
1	Dioxime‡	Small	60	1510	600	55
		Small	120	1660	600	65
		Large	60 and 120	Samples pitted		—
		Large	180	1380	540	51
2	Sulphur	Small	120	1030	760	47
		Small	180	1100	860	48
		Small	240	1260	670	48
		Large	120	1000	730	43
		Large	180	1090	900	47
		Large	240	1160	700	50

* Copolymer E64 Prepared in Expt. 9, Table III of Reference 3.
† Dimensions: 6- by 6- by 0.075-inch and 4- by 4- by 0.032-inch.
‡ Dioxime (GMF) recipe: polymer, 100; red lead, 10; zinc oxide, 5; stearic acid, 3; quinone dioxime, 2; and Furnex beads, 30.
§ Sulphur recipe: polymer, 100; Captax, 0.5; zinc oxide, 10; stearic acid, 2; sulpuhr, 2; Furnex beads, 30; and Tuads, 1.

Viscosity of Toluene-Acrylic Resin Solutions

The viscosity of solutions containing about 0.05-gram of polymer per 100 milliliters of toluene was determined at 25° C. (constant-temperature bath) with a modified Ostwald tube, and the natural logarithm of the relative viscsosity divided by concentration—that is, ($\ln \eta_r/c$)—was used as an index of the average molecular weight. As suggested by earlier workers,[10,11] viscosity data obtained with dilute solutions (Table 2 and Figure 1) are similar to those estimated by extrapolation to zero concentration, and hence are suitable for comparing average molecular weights.

TABLE 2. VISCOSITY DATA OBTAINED WITH TOLUENE SOLUTIONS OF AN ETHYL ACRYLATE-3-CHLOROPROPYL ACRYLATE COPOLYMER*

Concn., G. per 100 Ml. Toluene	$\frac{\ln \eta_r}{c}$	$\frac{\eta_{sp}}{c}$	η_{sp}	$k'\eta_{sp}$†	(η)
0.010	5.38	5.53	0.0553	0.0166	5.44
0.0138	6.16	6.43	0.0888	0.0266	6.26
0.0291	5.64	6.12	0.1782	0.0535	5.81
0.0463	5.79	6.64	0.3076	0.0923	6.08
0.0560	6.01	7.14	0.3997	0.120	6.38
0.1110	5.63	7.82	0.8676	0.260	6.21
0.1542	5.53	8.72	1.3445	0.403	6.22
0.2940	4.92	11.06	3.2531	0.976	6.00
0.0604‡	3.17	3.50	...	...	...

* Copolymer E78 prepared in Expt. 8, Table III, reference 3.
† $k' = 0.30$.
‡ Solvent: ethyl acetate.

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[2] Eastern Regional Research Laboratory, Philadelphia, Pa., Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.
[3] W. C. Mast, C. E. Rehberg, T. J. Dietz, and C. H. Fisher, *Ind. Eng. Chem.*, 36, 1022 (1944).
[4] W. C. Smith, Lee T. Smith, and C. H. Fisher, *Ibid.*, 36, 1027 (1944); 37, 365 (1945).
[5] C. E. Rehberg, W. A. Faucette, and C. H. Fisher, *J. Am. Chem. Soc.*, 66, 1723 (1944).
[6] "Organic Accelerators of the Vulcanization of Rubber," 16 pp., War Production Board, Office of the Rubber Director, Washington (Feb. 15, 1943).
[7] "A GR-S Vulcanization Catalyst," A. A. Somerville. Paper presented before the Division of Rubber Chemistry, A.C.S., New York, N. Y., Apr. 26, 1944.
[8] B. M. Sturgis and J. H. Trepagnier, *Rubber Age (N. Y.)* 54, 325 (1944).
[9] F. J. Van Antwerpen, *Ind. Eng. Chem.*, 35, 126 (1943).
[10] P. J. Flory, *J. Am. Chem. Soc.*, 65, 372 (1943).
[11] M. L. Huggins, *Rubber Chem. Tech.*, 17, 38 (1944).

With more concentrated solutions (having a relative viscosity of 1.4 or greater, the equation $\frac{\eta_{sp}}{c} = [\eta]\ (1 + k'\eta_{sp})$ proposed by Huggins[11] allows for corrections over a wide range of concentration.

Nature and Proportion of Haloalkyl Groups

In agreement with the generalization that bromine compounds are usually more reactive chemically than their chlorine analogs, copolymers of 2-bromoethyl or 3-bromopropyl acrylate vulcanized more rapidly than the copolymers containing comparable amounts of chlorine (Tables 3 and 4). A copolymer prepared from 95% ethyl acrylate, 4% 3-chloropropyl acrylate, and 1% 2-bromoethyl acrylate copolymer cured almost as rapidly as the copolymer containing 5% bromoethyl acrylate (Table 4, Expts. 8 and 9). This indicates that only a small proportion of the relatively expensive

Table 3. Preparation of Halogen-Containing Acrylic Resins

Expt. No.	Ethyl Acrylate, G.	Other Monomer, G.	Water, Ml.	Tergitol Paste No. 4 G.	Triton 720, G.	$(NH_4)_2S_2O_8$, G.	Temp., ° C.	Time, Hrs.	Yield, %	$\frac{\ln \eta_r}{C}$
1	1140	2-Chloroethyl acrylate, 60	2700	30	15	0.015	81–92	2.25	*	5.08
2	180	2-Chloroethyl acrylate, 20	400	3	6	0.01	81–92	1.5	86	3.60
3	170	2-Chloroethyl acrylate, 30	400	3	6	0.005	82–91	0.75	71	3.85
4	160	2-Chloroethyl acrylate, 40	400	3	6	0.005	82–91	0.75	94	3.58
5	180	3-Chloropropyl acrylate, 20	400	6	3	0.035	78–85	2.5	65	4.10
6	0	3-Chloropropyl acrylate, 100	200	3	1.5	0.01	98	1	92	Toluene insol.
7	180	3-Chloropropyl acrylate, 10; Acrylonitrile, 10	400	6	3	0.05	82–97	5.5	95	Toluene insol.
8	190	3-Chloropropyl acrylate, 8; 2-Bromoethyl acrylate, 2	400	6	3	0.01	83–91	1.75	80	..
9	190	2-Bromoethyl acrylate, 10	400	6	3	0.01	82–91	1.75	87	Toluene insol.
10	186	3-Bromopropyl acrylate, 14	400	3	6	0.005	82–92	1	90	4.79
11	190	1,3-Dichloro-2-propyl acrylate, 10	400	3	6	0.01	82–95	1.5	97	4.80
12	180	1,3-Dichloro-2-propyl acrylate, 20	400	3	6	0.01	82–94	1.5	94	4.37 4.60

* Emulsion mixed with other batches; yield not determined.

Table 4. Vulcanization of Various Halogen-Containing Acrylic Resins*

Expt. No.	Monomers, % Ethyl Acrylate	Monomers, % Other Monomer	Vulcanizing Recipe	Curing Time at 298° F., Min.	Tensile Strength, P.S.I.	Elongation, %	Shore A Hardness	Toluene, 50-Heptane, 50, Weight Increase, %	Modulus at 300%	Modulus at 400%	Modulus at 500%	Modulus at 600%
1	95	Chloroethyl Acrylate, 5	Sulphur	180	890	1100	37	..	50	110	170	250
				240	1430	860	48	..	160	370	570	750
2A	90	Chloroethyl Acrylate, 10	Dioxime†	60	1140	600	38	..	550	830	1010	1140
				120	1210	490	47	..	660	954	1280	..
				180	1480	490	43	16	910	1190	1600	..
2B	90	Chloroethyl Acrylate, 10	Sulphur‡	120	950	820	30	..	160	250	400	550
				180	1330	760	32	..	210	330	610	870
				240	1380	650	35	16	270	580	900	1140
3A	85	Chloroethyl Acrylate, 15	Dioxime	30	1170	660	36	..	310	550	800	940
				60	1330	670	39	16	370	730	1010	1160
				120	1230	520	46	..	510	880	1170	..
3B	85	Chloroethyl Acrylate, 15	Sulphur	120	1230	830	34	..	170	300	450	690
				180	1220	490	38	15	590	980	1280	..
4A	80	Chloroethyl Acrylate, 20	Dioxime	30	1270	680	43	..	..	..	..	..
				60	1290	560	40	15	560	1120	..	..
				120	1430	420	43	..	930	1270	..	..
4B	80	Chloroethyl Acrylate, 20	Sulphur	120	1280	520	41	14	570	940	1220	..
				180	760	90	64	..	..	..	..	..
5	90	Chloropropyl Acrylate, 10	Dioxime	60	1500	550	59	..	510	940	1340	..
				120	1420	430	64	..	740	1210	..	..
				180	1550	420	62	..	900	1490	..	..
6A	0	Chloropropyl Acrylate, 100	Sulphur	15	530	860	31	..	..	80	160	230
				30	770	730	38	12	60	190	290	430
				60	890	350	50	..	660	..	..	..
6B	0	Chloropropyl Acrylate, 100	Sulphur	5 (320° F.)	650	80	59	..	..	..	..	..
				10 (320° F.)	660	80	68	..	..	..	..	..
				15 (320° F.)	620	70	70	..	..	..	..	..
7A	90	Chloropropyl Acrylate, 5; Acrylonitrile, 5	Dioxime	60	1440	520	60	..	580	1020	1390	..
				120	1550	460	61	..	900	1280	..	..
				180	1640	410	69	..	1110	1600	..	..
7B	90	Chloropropyl Acrylate, 5; Acrylonitrile, 5	Sulphur	120	1310	640	51	..	360	620	910	1180
				180	1420	600	53	..	460	790	1080	1370
8A	95	Chloropropyl Acrylate, 4; Bromoethyl Acrylate, 1	Dioxime	30	1300	500	50	..	660	1040	1300	..
				60	1490	520	58	..	1030	1335	1480	..
				120	1390	340	60	..	1220	..	..	..
8B	95	Chloropropyl Acrylate, 4; Bromoethyl Acrylate 1	Sulphur	60	1170	770	43	..	200	360	580	840
				120	1370	730	40	..	180	380	670	990
				180	1650	680	44	..	300	660	1020	1350
9A	95	Bromoethyl Acrylate, 5	Dioxime	30	1410	640	49	..	520	810	1060	1320
				60	1510	520	48	21	660	1150	1360	..
				120	1520	400	51	..	1080	1570	..	..
9B	95	Bromoethyl Acrylate, 5	Sulphur	30	1170	990	38	..	70	150	230	340
				60	1190	840	39	..	90	190	340	590
				120	1390	860	43	25	100	180	290	540
10A	93	Bromopropyl Acrylate, 7	Dioxime	30	940	270	55	..	..	..	..	..
				60	920	170	59	..	..	..	..	..
				120	820	120	65	..	..	..	..	..
10B	93	Bromopropyl Acrylate, 7	Sulphur	30	1350	700	34	..	..	..	..	..
				60	1150	470	39	..	..	..	..	..
				120	1120	310	44	..	..	..	..	..
11A	95	Dichloroisopropyl Acrylate, 5	Dioxime	60	1250	580	50	..	440	890	1080	..
				120	1420	540	55	..	780	1060	1300	..
				180	1500	480	55	..	980	1260	1540	..
11B	95	Dichloroisopropyl Acrylate, 5	Sulphur	180	1220	730	47	..	..	..	..	..
12A	90	Dichloroisopropyl Acrylate, 10	Dioxime	60	1290	560	45	..	..	..	..	.
				120	1410	490	47	..	..	..	..	.
				180	1450	460	49	..	..	..	..	..
12B	90	Dichloroisopropyl Acrylate, 10	Sulphur	120	1260	720	45	..	200	390	640	950
				180	1310	470	51	..	670	1070	1400	..

* Preparation given in Table 3.
† Standard quinone dioxime recipe: polymer, 100; red lead, 10; zinc oxide, 10; stearic acid, 3; quinone dioxime, 2; and Furnex beads, [illegible].
‡ Standard sulphur recipe: polymer, 100; Rotax, 0.5; zinc oxide, 10; stearic acid, 2; sulphur, 2; Furnex beads, 30; and Tuads, 1.

bromine-containing monomer is required for more rapid vulcanization when used in conjunction with chloropropyl acrylate.

The 100% chloropropyl acrylate polymer and the 7% bromopropyl acrylate copolymer cured much more rapidly than the other halogen-containing polymers (Table 4). In addition to supplying further evidence that bromine-containing acrylic resins vulcanize readily, these experiments indicate that the amount of halogen as well as its nature influences the vulcanization rate (Figures 2 and 3). The vulcanizates prepared from the 100% chloropropyl acrylate polymer and the 7% bromopropyl acrylate copolymer had lower tensiles and elongations than the vulcanizate of the 10% chloropropyl acrylate copolymer.

Preliminary experiments conducted in this laboratory indicated that polymers suitable for vulcanization can be prepared by halogenation of polyethyl acrylate. The location of the halogen in the polymer was not determined.

Because of the increased cost of acrylic resins containing appreciable quantities of bromine and the fact that vulcanizates prepared from bromine-containing copolymers would not be expected to have improved physical properties (Table 4), this investigation was largely concerned with the development of satisfactory methods of vulcanizing chlorine-containing acrylic resins.

Vulcanization at Higher Temperature

Copolymers prepared by polymerizing ethyl acrylate with 5% of either 2-chloroethyl or 3-chloropropyl acrylate were used in a brief study of the effect of temperature and certain variations in compounding on the vulcanization (Tables 5 and 6).

TABLE 5. VULCANIZATION OF 95% ETHYL ACRYLATE—5% CHLOROPROPYL ACRYLATE COPOLYMER*

Expt. No.	Vulcanization Recipe	Additional Ingredients, Parts per 100 Parts of Polymer	Curing Time at 298° F., Min.	Tensile Strength P.S.I.	Ultimate Elongation, %	Shore A Hardness	Permanent Set, % At Break	Permanent Set, % 10 Min.	Modulus at 600%
1	Quinone Dioxime†	ZnO, only 5	60	1530	650	55	25.5	34.9	1450
			60 (307°)	1580	590	58	17.6	..	..
			120	1610	560	63	41.2	..	..
2	Quinone Dioxime	Micronex Beads, 5	120	1540	500	57	..	..	960 (300%)
			180	1530	390	54	..	..	1170 (300%)
			240	1580	360	58	..	..	1360 (300%)
3	Quinone Dioxime	Micronex Beads, 10	120	1540	490	60	..	..	920 (300%)
			180	1670	390	57	..	..	1420 (300%)
			240	1580	350	65	..	..	1460 (300%)
4	Quinone Dioxime	Micronex Beads, 15	180	1870	330	73	..	..	..
			240	1740	270	71	..	..	..
			300	1820	230	80	..	..	..
5	Sulphur‡	——	180	990	950	46	17.6	..	540
			120 (312°)	1130	880	50	15.7	33.3	700
			180 (312°)	1210	790	48	13.7	21.4	830
			180 (320°)	1210	790	48	16.9	22.7	810
6	Sulphur‡	Triethylene Tetramine, 0.5	60	1060	930	40	..	..	350
			120	1460	740	41	..	..	1030
			180	1530	640	44	..	..	1380
7	Sulphur‡	Plasticizer KP140, 5; Furnex, 50	180	1080	670	48	..	..	980
			240	1210	660	50	..	..	1140
			360	1290	510	57	..	..	..
8	Sulphur‡	Plasticizer KP140, 10; Furnex, 50	180	990	850	42	..	..	470
			240	1050	780	41	..	..	690
			360	1180	670	48	..	..	1090
9	Sulphur‡	Plasticizer KP140, 20; Furnex, 75	240	790	670	47	..	..	750
			360	920	540	50	..	..	..
10	Sulphur‡	Santicizer E15, 5; Furnex, 50	360	1240	590	55	..	..	1240
11	Sulphur‡	Cuprax, 0.5; Cumate, 1§	300	1500	760	50	..	..	..
12	Amine¶	——	60	1080	290	48	..	..	..
			120	970	260	49	..	..	..
			180	1050	230	53	..	..	..
13	Polyac**	Polyac, 1	120	870	880	36	..	..	360
			180	1310	880	35	..	..	750
			300	1460	700	41	..	..	1180
14	Polyac**	Polyac, 2	120	1450	820	40	..	..	420
			180	1540	770	46	..	..	910
15	Polyac**	Polyac, 2	60 (320°)	1490	650	43	..	..	1320
			120 (320°)	1470	490	45	..	..	..
16	Polyac**	Polyac, 2; Tuads, 1	60	790	950	39	..	..	310
			120	1370	730	41	..	..	1020
17	Polyac**	Polyac, 3	120	1290	830	41	..	..	660
			180	1390	710	40	..	..	1110

* Copolymer E78 prepared in Expt. 8, Table 3 of reference [3].
† Standard quinone dioxime recipe: copolymer, 100; red lead, 10; zinc oxide, 10; stearic acid, 3; quinone dioxime, 2; Furnex beads, 30.
‡ Standard sulphur formula: copolymer, 100; Rotax, 0.5; zinc oxide, 10; stearic acid, 2; sulphur, 2; Furnex beads, 30; and Tuads 1.
§ Cuprax and Cumate substituted for Rotax and Tuads.
¶ Copolymer, 100; calcined magnesia, 10; zinc oxide, 10; stearic acid, 2; triethylene tetramine, 1; Furnex beads, 30.
** Copolymer, 100; zinc oxide, 10; stearic acid, 2; Polyac, 1 to 3; Furnex beads, 30.

TABLE 6. VULCANIZATION OF CHLORINE-CONTAINING ACRYLIC RESINS

Expt. No.	Monomers, % Ethyl Acrylate	Monomers, % Chloroalkyl Acrylate	Vulcanizing Recipe	Deviations from Standard Formula	Curing Time at 298° F., Min.	Tensile Strength P.S.I.	Ultimate Elongation, %	Shore A Hardness	Modulus	Permanent Set, %
1*	95	Chloroethyl, 5	Sulphur†	Cuprax, 0.5; Kosmos, 50	240	1130	750	65	800 (600%)	60.1
					360	1250	660	65	1000 (600%)	
2*	95	Chloroethyl, 5	Dioxime‡	Kosmos, 50	120	1640	480	69	....	19.6
					180	1750	390	76	....	21.8
					240	1730	370	77	....	18.4
3*	95	Chloroethyl, 5	Dioxime	Red lead, 20; Dioxime, 4; Kosmos, 50	60	1540	410	79	....	24.9
					120	1750	310	85	....	32.9
					180	1850	270	91	....	34.5
4§	95.1	Chloropropyl, 4.9	Dioxime	ZnO, 5	120 (303°)	1560	510	65	1410 (400%)	31.8
					150 (303°)	1610	470	67	1540 (400%)	32.9
					210 (303°)	1620	390	66	....	..
					45 (312°)	1300	580	51	970 (400%)	16.7
					60 (312°)	1460	540	58	1200 (400%)	20.2
5§	95.1	Chloropropyl 4.9	Sulphur	——	210 (312°)	1240	950	39	630 (600%)	..
					240 (312°)	1200	890	42	680 (600%)	..
					300 (307°)	1280	760	44	880 (600%)	..
					180	890	1150	39	280 (600%)	..
					240	1030	850	42	580 (600%)	..

* Copolymer E73 prepared from 95% ethyl acrylate and 5% 2-chloroethyl acrylate (Expt. 12, Table 3, reference [3]).
† Sulphur recipe: Copolymer, 100; Rotax, 0.5; Zinc Oxide, 10; stearic acid, 2; sulphur, 2; Furnex beads, 30; Tuads, 1.
‡ Dioxime recipe: Copolymer, 100; red lead, 10; zinc oxide, 10; stearic acid, 3; quinone dioxime, 2; Furnex beads, 30.
§ Copolymer E61 (Expt. 7, Table 3, reference [3]).

As would be expected, vulcanization occurred more rapidly when higher temperatures were used with the dioxime, sulphur, or Polyac recipes (Table 5, Expts. 1, 5, and 15; Table 6, Expts. 4 and 5), but at least 60 minutes was required even at the higher temperatures; moreover, relatively high temperatures are sometimes objectionable; for example, pitting occurs when temperatures appreciably above 298° F. are used with the dioxime recipe. Therefore, although higher temperatures may be used satisfactorily in some instances to increase the rate of vulcanization, other methods of achieving rapid curing are needed.

Miscellaneous Compounding Recipes

The desirability of having rapid methods of curing became more apparent when plasticizers and harder carbon blacks were included in the compounding recipes. Plasticizers and blacks had the expected softening and stiffening effect, respectively, on the vulcanizates, but they made the time required for curing too long (Tables 5 and 6).

Although satisfactory vulcanizates were obtained with Cuprax-Cumate and Polyac recipes, these active accelerators did not effect material shortening of the curing period.

Increased quantities of red lead and quinone dioxime appeared to accelerate the curing of a 5% chloroethyl acrylate copolymer (Table 6, Expt. 3), but the permanent set was increased.

Experiments conducted with a 10% 3-chloropropyl acrylate copolymer showed that stearic acid in the standard sulphur-Rotax-Tuads formula (Table 7, Expts. 1 and 3) increases tensile strength slightly. Phenylstearic acid also appeared to be beneficial (Table 7, Expt. 2); the 120- and 180-minute vulcanizates were softer and stronger than the corresponding stearic acid vulcanizates.

A 10% 3-chloropropyl acrylate copolymer was cured in 30 minutes at 312° F. by omitting stearic acid and zinc oxide and using sulphur-Rotax-Tuads and sulphur-Monex combinations (Table 7, Expts. 5 and 6). It is planned to study such recipes further to determine whether 95% ethyl acrylate-5% chloroalkyl acrylate copolymers also can be cured rapidly under these conditions.

Attempts to accelerate the curing of a 95.2% ethyl acrylate-4.8% 3-chloropropyl acrylate copolymer (prepared in Expts. 3 and 4 of Table 3 of reference [3]) by substituting two parts of Du Pont No. 8, Polyac, Safex, Tuads, 2MT, or Texas for one part of Tuads in the standard sulphur-Rotax-Tuads formula (given in footnote § of Table 1) were unsuccessful because pitted specimens were obtained. Possibly satisfactory vulcanizates would be obtained by using only one part of the accelerators or by omitting the zinc oxide and stearic acid, but these possibilities were not studied.

The vulcanizate obtained by curing 100 parts of a 95.2% ethyl acrylate-4.8% 2-chloroethyl acrylate copolymer (Table 3, Expt. 14 of reference [3]) with Rotax, 0.5-part; zinc oxide, 5; stearic acid, 3; sulphur, 3; Furnex beads, 25; Micronex Beads, 20; R2 Crystals, 2; and Selenac, 0.75 at 298° F. for 180 minutes had the following properties: tensile, 970 p.s.i.; ultimate elongation, 970%; and Shore A hardness, 55. Hence use of considerable amounts of several accelerators cannot be relied upon to result in rapid curing or a good vulcanizate.

Effect of Amines

Various amines were used as curing ingredients because it was considered likely that the amines, unlike the inorganic oxides, would be appreciably soluble in the copolymer and therefore be well dispersed and in better condition for reacting with the halogen atoms in the polymer. It was believed that the amines might transform the chloroalkyl groups into vulcanizable olefinic linkages by dehydrohalogenation or form cross-links through newly created nitrogen-carbon bonds, thus either facilitating or actually effecting vulcanization. Experiments carried out with several amines demonstrated that these expectations were justified.

Triethylene tetramine was a powerful accelerator when used as an additional ingredient with either the sulphur or the dioxime recipe, as little as 0.5 part being effective (Table 8). The accelerating effect was roughly proportional to the percentage of triethylene tetramine used (Figure 4). The Shore A hardness of the sulphur vulcanizates increased with the proportion of the amine; whereas the hardness of the dioxime vulcanizates was decreased by 0.5- to one part of amine, but increased by larger quantities (Figure 4). On the basis of these results, 0.5- to one and one part, respectively, of triethylene tetramine per 100 parts of polymer were selected for general use as accelerator with the dioxime and sulphur-Rotax-Tuads recipes.

Triethylene tetramine was effective as an accelerator for both 5% and 10% 3-chloropropyl acrylate copolymers (Table 5, Expt. 6) and when Kalvan (calcium carbonate) instead of carbon black was used as reenforcing agent (Table 7, Expt. 4). Triethylene tetramine was used successfully also as the sole vulcanizing agent (Table 8, Expts. 21 and 22). When triethylene tetramine is used as an additional ingredient in the sulphur and dioxime recipes, presumably the amine functions both as a

TABLE 7. VOLCANIZATION OF A 90% ETHYL ACRYLATE—10% CHLOROPROPYL ACRYLATE COPOLYMER* WITH VARIOUS RECIPES

Expt. No.	Compounding Ingredients, Parts per 100 Parts of Copolymer: Rotax	ZnO	Sulphur	Furnex	Tuads	Stearic Acid	Kalvan	Miscellaneous	Curing Conditions: Temp., ° F.	Time, Min.	Tensile P.S.I.	Ultimate Elongation, %	Shore A Hardness
1	0.5	10	2	30	1	2	0	——	298	60	1030	830	48
									298	120	1110	720	52
									298	180	1260	640	50
2	0.5	10	2	30	1	0	0	Phenylstearic acid, 2	298	60	870	1020	26
									298	120	1140	870	30
									298	180	1320	770	32
3	0.5	10	2	30	1	0	0	——	298	60	1010	780	45
									298	120	1160	690	48
									298	180	1180	540	48
4	1	0	2	0	1	0	80	Triethylene tetramine, 1	312	30	1080	360	52
									312	60	1170	230	67
									312	120	920	160	69
5	1	0	2	0	1	0	80	——	312	30	1060	590	50
									312	60	1000	360	56
									312	120	940	250	63
6	0	0	2	0	0	0	80	Monex, 1	312	30	1300	600	53
									312	60	1190	420	58
									312	120	900	260	67
7	0.5	0	2	30	1	0	0	——	312	30	1350	680	42
									312	60	1170	430	43
									312	120	1260	420	45
8	0	10	0	30	0	3	0	Red lead, 10; quinone dioxime, 2; triethylene tetramine, 1; magnesia, 5	312	5	1120	460	46
									312	10	990	400	51
									312	15	1010	330	52
									320	5	940	540	52
									320	10	770	430	52
									320	15	990	360	55
9	0.5	10	2	30	1	2	0	Triethylene tetramine, 1; calcined magnesia, 5	312	5	1470	630	51
									312	10	1460	530	50
									312	15	1350	470	52
									320	5	1260	510	52
									320	10	1420	360	47
									320	15	1330	460	53

* Copolymer E218 prepared under conditions similar to those outlined in Table 3.

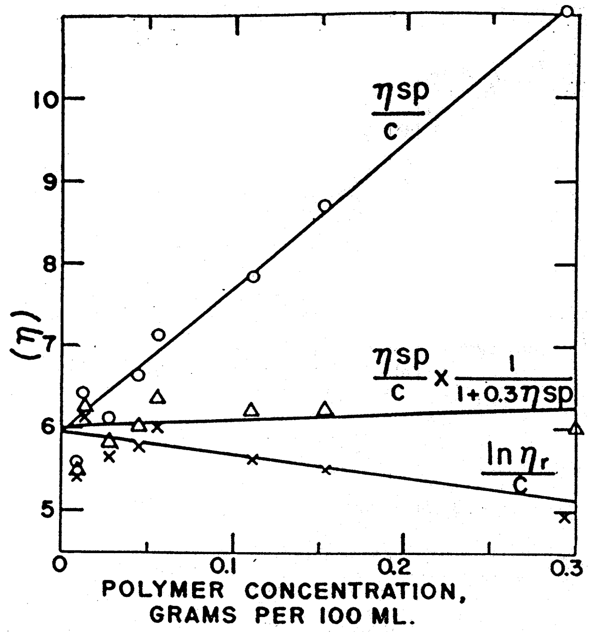

Fig. 1. Viscosity Data Obtained with Toluene Solutions of an Ethyl Acrylate-Chloropropyl Acrylate Copolymer

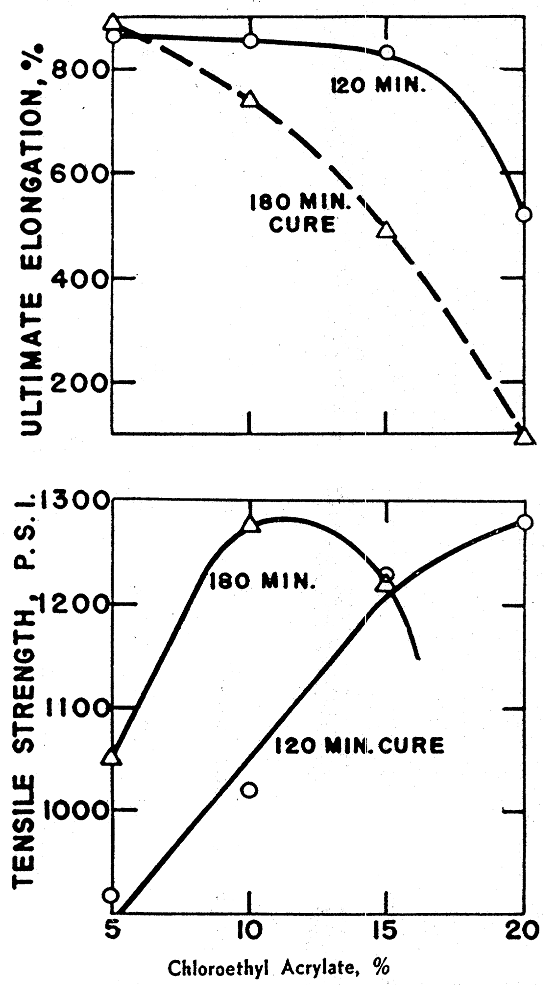

Fig. 2. Effect of Chloroethyl Acrylate Content on Properties of Sulphur-Vulcanized Ethyl Acrylate-Chloroethyl Acrylate Copolymers

vulcanizing agent and as an accelerator for sulphur and dioxime vulcanization.

By using triethylene tetramine and calcined magnesia as additional ingredients and higher curing temperatures, it was possible to vulcanize a 10% 3-chloropropyl copolymer in five minutes by either the sulphur-Rotax-Tuads or the dioxime recipe (Table 7, Expts. 8 and 9).

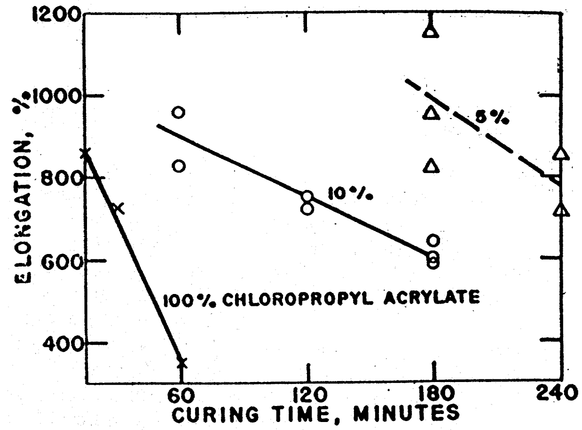

Fig. 3. Ultimate Elongation of Sulphur-Vulcanized Ethyl Acrylate-Chloropropyl Acrylate Copolymers

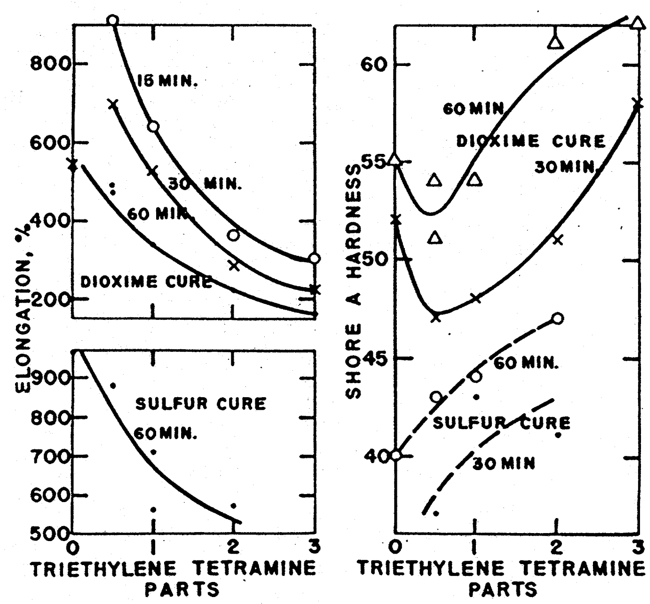

Fig. 4. Effect of Triethylene Tetramine on the Vulcanization of a 90% Ethyl Acrylate-10% Chloropropyl Acrylate Copolymer

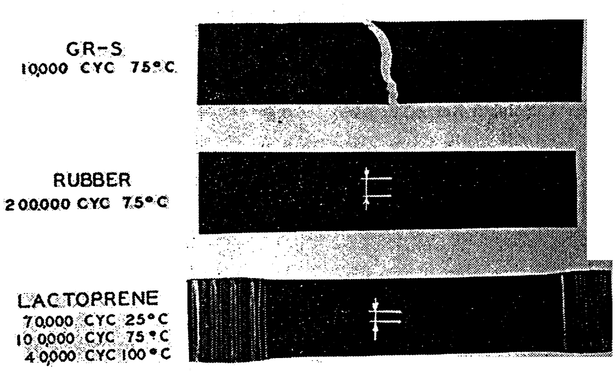

Fig. 5. Cut-Growth Resistance of GR-S, Natural Rubber, and Lactroprene Vulcanizates

Other amines, including p-phenylene diamine and n-butyl ethanolamine, accelerated curing when used in conjunction with the sulphur-Rotax-Tuads recipe (Table 8, Expts. 17 to 20). Presumably, many other amines would function in a similar manner, and possibly some of them would be superior to those used in the present study.

Magnesium oleate and magnesium phenylstearate also were used as additional ingredients with the sulphur-Rotax-Tuads recipe to determine whether these compounds would be similar to amines in accelerating the vulcanization. The magnesium salts had little or no accelerating effect, but the magnesium phenylstearate decreased the Shore A hardness and increased the tensile strength and elongation (Table 8, Expts. 13 to 16).

Properties of the Vulcanizates

Various data on tensile strength, elongation, Shore A hardness, oil resistance, and permanent set were given in a previous paper.[3] The abrasion resistance of a vulcanizate prepared from a 95% ethyl acrylate-5% 2-chloroethyl acrylate (Expt. 12, Table 3, reference [3]) is shown below. The copolymer was vulcanized at 298° F. for 120 minutes with quinone dioxime and red lead, and the test was made by A.S.T.M. Method B, in which the National Bureau of Standards abrader is used. Possibly the abrasion resistance (approximately 50% of the natural rubber standard) of acrylic vulcanizates can be improved by different compounding and curing conditions.

Abrasion Resistance of Acrylic Vulcanizates*

	Acrylic Vulcanizate	A.S.T.M. Comparison Standard B
Cycles required to abrade 0.1-inch..........	325	620
Specific gravity	1.445	1.18
Volume loss per 1,000 cycles, cc............	5.61	2.72
Abrasion resistance, % of comparison standard	48.5	...

* The copolymer (100 parts) was compounded as follows: red lead, 10, zinc oxide, 10; stearic acid, 3; quinone dioxime, 2; and Kosmos, 50. Properties: tensile, 1640 p.s.i.; ultimate elongation, 480%; Shore A hardness, 69; and permanent set, 19.6%.

A test made with an acrylic vulcanizate at the National Bureau of Standards indicates that Lactoprene has unusually good flex life and cut-growth resistance. The vulcanizate was prepared from a 95% ethyl acrylate-5% 3-chloropropyl acrylate copolymer (Table 3, Expt. 7, reference [3]). The quinone dioxime formula (Table 1, footnote ‡) was used, and the compounded material was cured at 298° F. for 120 minutes. Even after being

Table 8. Vulcanization of 90% Ethyl Acrylate—10% 3-Chloropropyl Acrylate Copolymer*

Expt. No.	Vulcanization Recipe	Additional Ingredients, Parts per 100 Parts of Polymer: Triethylene Tetramine	Miscellaneous	Curing Conditions: Temp., ° F.	Time, Min.	Tensile Strength, P.S.I.	Ultimate Elongation, %	Shore A Hardness	Modulus at 600%
1	Quinone dioxime-red lead†	0		298	30	990	540	52	..
				298	60	1360	530	55	..
				298	120	1450	410	58	..
2		0.5		298	15	1240	910	43	660
				298	30	1350	700	47	1150
				298	60	1370	470	51	...
				298	120	1340	310	58	..
3		0.5		298	60‡	1340	490	54	..
4		1		298	15	1350	640	44	..
				298	30	1360	530	48	..
				298	60	1350	340	54	...
5		2		298	15	1200	360	48	..
				298	30	1160	280	51	..
				298	60	1270	220	61	..
6		3		298	15	950	300	53	..
				298	30	920	220	58	..
				298	60	950	160	62	..
7	Sulphur-Rotax-Tuads§	0		298	60	910	960	40	320
				298	120	1370	750	44	990
				298	180	1390	600	47	1390
8		0.5		298	30	320	1210	37	..
				298	60	1290	880	43	..
				298	120	1360	560	48	..
9		1		298	15	1460	830	42	..
				298	30	1210	730	43	..
				298	60	1380	710	44	..
				312	15	1120	>1100	33	..
				312	30	1420	790	38	..
				312	60	1370	460	45	..
10		2		298	15	910	>1100	40	..
				298	30	1290	1110	41	..
				298	60	1380	570	47	..
11		0.5	MgO, 5; (ZnO, only 5)................	298	15	930	1150	41	..
				298	30	1150	880	43	..
				298	60	1270	730	47	..
12		0.5	MgO, 10; (ZnO, only 5)................	298	15	930	830	42	..
				298	30	1090	800	45	..
				298	60	1200	570	48	..
13		0	Mg oleate, 5..........................	298	120	1180	940	42	..
				298	180	1320	680	44	..
14		0.5	Mg oleate, 5..........................	298	60	1200	870	42	..
				298	120	1230	730	44	..
15		0	Mg phenylstearate, 5..................	298	60	680	1320	30	..
				298	120	1320	1000	33	..
				298	180	1480	770	36	..
16		0.5	Mg phenylstearate, 5..................	298	30	1530	1340	33	..
				298	60	1550	1010	34	..
				298	120	1620	760	38	..
17			p-Phenylene diamine, 2................	298	30	1220	660	40	..
				298	60	1060	410	44	..
				298	120	1070	280	50	..
18			Triethylene tetramine, 2..............	298	15	910	>1100	40	..
				298	30	1290	1110	41	..
				298	60	1380	570	47	..
19			Di-n-butylaminoethanol, 1	298	30	..	>1200	33	..
				298	60	..	>1200	36	..
				298	120	1270	730	40	..
20			n-Butyl ethanolamine, 2...............	298	30	1330	1090	34	..
				298	60	1390	800	38	..
				298	120	1370	530	41	..
21	(S, Rotax, and Tuads omitted)		MgO, 10; ZnO, 10; stearic acid, 2; triethylene tetramine, 0.5; Furnex, 30....	312	15	1410	630	40	..
				312	30	1410	480	43	..
				312	60	1240	320	43	..
22	(S, Rotax, and Tuads omitted)		MgO, 10; ZnO, 10; stearic acid, 2; triethylene tetramine, 1; Furnex 30......	298	30	1420	620	43	..
				298	60	1320	430	48	..
				298	120	1080	280	53	..
23	(S and Rotax omitted)		ZnO, 10; stearic acid, 2; Polyac, 2; Furnex, 30; Tuads, 1....................	320	15	1280	420	42	..
				320	30	1090	390	44	..
				320	60	1490	570	41	..

* Copolymer E170 prepared under the conditions outlined in Table 3.
† Standards quinone dioxime formula (Table 4, footnote †).
‡ Crescent tear strength, 134 lb. per in.; permanent set, 11.5%.
§ Standard sulphur-Rotax-Tuads formula (Table 4, footnote ‡).

flexed in the De Mattia machine for 70,000 cycles at 25°, 100,000 cycles at 75°, and 40,000 cycles at 100° C., the cut or slit in the acrylic vulcanizate had not grown, although the specimen displayed considerable permanent set (Figure 5). Natural rubber and GR-S samples of comparable loading also were tested; there was some cut growth with the natural rubber specimen; whereas the GR-S sample failed entirely (Figure 5).

It was shown in a recent paper[3] that the brittle point of Lactoprene, determined by the method of Selker, Winspear, and Kemp,[12] can be lowered by blending with isobutylene copolymer (Butyl rubber). The brittle point can be lowered also by a plasticizer. When an ethyl acrylate-3-chloropropyl acrylate copolymer was plasticized with five, ten, and 20 parts of Plasticizer SC, the brittle points of the vulcanizates (Compounds 2, 3, and 4, Table 6, reference [3]) were —19°, —25°, and —31° C., respectively. It is planned to study this subject further to determine suitable types and proportions of plasticizers for lowering the brittle point of acrylic elastomers.

All the acrylic vulcanizates (prepared from essentially methyl or ethyl acrylate polymers) have had excellent resistance to paraffins and moderately good resistance to a 50-50 mixture of toluene and heptane. Resistance to aromatics was appreciably increased by using 10% or more haloalkyl acrylate in the emulsion polymerization (Table 4).

It was shown in a previous paper that acrylic vulcanizates have good heat-aging properties.[3]

The authors are grateful to C. E. Rehberg for supplying the haloalkyl acrylates and to Lynn G. Filachione and William E. Palm for assistance in preparing and evaluating the elastomers.

[12] M. L. Selker, G. G. Winspear, and A. R. Kemp, *Ind. Eng. Chem.*, **34**, 156 (1942).